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New Applications of Ionization and Flourescence Techniques for Detecting and Characterization of Open-shell Organometallics in the Gas Phase

by

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New Applications of Ionization and Fluorescence Techniques for Detection and Characterization of Open-shell Organometallics in the Gas Phase

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Recent advances are discussed in the development of electronic spectroscopic probes for the study of excited-state structure and photodissociation dynamics of gas-phase organometallics. Because of the short timescale for intermolecular energy transfer within van der Waals clusters, the UV photodissociation dynamics of cluster-bound transition metal carbonyls differs considerably from the photodissociation dynamics of the naked species in the gas phase. It is therefore possible to employ multi-photon ionization to produce cluster-bound metal carbonyl photoions in high yield. Resonant photoionization (accomplished with tunable lasers) and mass-resolved detection allow one to probe the excited states of both closed-shell and open-shell neutral organometallics. Finally, a time-resolved two-laser technique employing fluorescent detection of atomic photoproducts is described. This technique allows one to study photodissociation dynamics of organometallics with a temporal resolution competitive with the fastest transient absorption techniques, and a level of sensitivity which is far superior.

Coordinatively unsaturated organotransition metal species play a central role in mechanistic organometallic chemistry. Such species are important both in stoichiometric reactions (1,2) and, perhaps more importantly, in a wide range of catalytic reactions: for

example, synthetically important hydrogenation reactions (3); industrially important hydroformylation (4) and polymerization reactions (5); automotive engine combustion control and emission reduction (6); and biologically important processes such as nitrogen fixation (7) and oxygen transport (8). It has been suggested that the single most important property of a homogeneous catalyst is a vacant coordination site (9). Clearly, the production of model coordinatively unsaturated species in the laboratory, and the development of fast, sensitive probes for detection and characterization of these species, impacts upon a broad scope of disciplines in the natural sciences.

A convenient route to the synthesis of coordinatively unsaturated molecules in the laboratory is the photolysis of appropriate saturated precursors by pulsed visible or UV laser irradiation. While single-quantum photodissociation in condensed phases is characterized exclusively by the breaking of a single bond and the production of a single site of coordinative unsaturation (10), photodissociation of a gas-phase molecule may lead to the breaking of several bonds (depending on the energy of the photon absorbed) and the production of multiple vacancies in the coordination sphere (11). These coordinatively unsaturated molecules are highly reactive: subject to the constraints of electronic spin conservation, they will undergo ligand recombination reactions in the gas phase at or near the gas-kinetic limiting rate (12), and will undergo coordination with solvent (or host) molecules in liquids and frozen matrices at diffusion-limited rates (13-19). In order to detect and characterize such highly reactive species, one must employ techniques which are sufficiently sensitive to allow detection at low number densities, and sufficiently fast to avoid interference from competing solvation and/or ligand recombination reactions.

Available Spectroscopic Probes for Organometallics

Vibrational Probes. One powerful method by which coordinatively unsaturated

species have been identified and studied is time-resolved IR absorption spectroscopy, or TRIS (20). Such experiments are typically performed by pulsed UV laser photodissociation of an appropriate saturated precursor in a gas cell. Transient changes in the attenuation of a continuous infrared beam passed down the length of the cell, due to disappearance of the saturated precursor and appearance of the various photoproducts following UV photolysis, are monitored by a fast IR detector. Primary photoproduct identities are usually assumed on the basis of results from gas-phase chemical trapping studies (11) as well as known transition frequencies from matrix isolation studies (21), while photoproduct geometries can often be inferred from group theoretical analysis of the number and relative intensities of IR absorption features (22).

While the application of TRIS has led to advances in our understanding of the structure and reactivity of coordinatively unsaturated organometallic species (primarily those in the electronic ground state), the technique is limited by a few significant constraints. First, because this is an *absorption* technique, the product of the number density and extinction coefficient of a target molecule must be large in order to allow for the molecule's detection. The large extinction coefficients associated with C-O stretching modes of metal carbonyls allow for detection of these species at low number densities, but weaker absorbers must be present at higher number densities. For sufficiently weak absorbers, required number densities are large enough that reactive bimolecular collisions may take place during the course of product detection, thus complicating spectral interpretation. Second, because one employs infrared detectors, the temporal resolution of transient experiments is limited. Typical detector/preamp combinations for this type of experiment display simple exponential risetime constants in the range from 100 to a few hundred nanoseconds (23). The microscopic details of processes which take place on a much shorter timescale cannot be directly probed. Finally, since TRIS is a purely *vibrational* spectroscopic probe, one is unable to distinguish directly between vibrational transitions taking place in the *ground* electronic

manifold and those taking place in an *excited* electronic manifold of the target molecule. The ability to make such a distinction is desirable, since one would expect that: (a) the excited states of coordinatively unsaturated organometallic species would represent a significant fraction of total photoproducts in some photophysical schemes, and (b) the structure and reactivity of electronically excited states of these species would differ significantly from those of the ground state.

Electronic Probes. Clearly, a spectroscopic technique which probes the *electronic* structure of coordinatively unsaturated organometallic species would allow the experimentalist to acquire information complementary to that provided by vibrational probes such as TRIS. However, interrogation of the electronic structure of these species is thwarted by the very property which makes them easy to produce and interesting to study in the first place; that is, the photolability of coordination compounds, both saturated and unsaturated. Electronic surface crossings among excited states of these molecules occur at rates which are often faster than those of optical transitions. Electronic relaxation generally occurs via non-radiative mechanisms and is often accompanied by the breaking of one or more metal-ligand bonds. Consequently, with a few notable exceptions (24-26), powerful techniques such as laser induced fluorescence (LIF) and multiphoton ionization (MPI) have not enjoyed general applicability to the study of electronic excited states of coordinatively unsaturated organometallic species.

The photodissociation behavior of organometallic molecules is clearly governed by the interplay between *intramolecular* energy partitioning, and *intermolecular* energy transfer. The photodissociation dynamics of these species evolves from behavior characteristic of the naked molecule (where energy disposal via bond cleavage predominates), to that characteristic of solvated molecules (where energy disposal via solvent heating predominates). By studying this behavioral evolution experimentally,

one can in principle derive detailed insights about the electronic structure of these transient excited species. Weakly bound van der Waals clusters represent a convenient, *finite* experimental model of the complex, virtually infinite environment of condensed matter. Such clusters can be easily formed by expanding a buffer gas such as helium, seeded with a small proportion (perhaps a fraction of a percent) of a compound of interest, into a vacuum chamber through an orifice of small diameter. The cluster beam thus produced is amenable to interrogation by a broad array of spectroscopic techniques.

An area of ongoing research in our laboratory at SUNY, Buffalo, is the photodissociation dynamics of organometallics bound within van der Waals clusters. The ultimate goal of this research is to provide a better understanding of excited electronic states of organometallic molecules, particularly those which are coordinatively unsaturated, and the roles of these excited states in mediating energy transfer. It is hoped that a better understanding of these phenomena will lead to the development of novel approaches for fast, sensitive detection and characterization of this important class of molecules.

Photodissociation Dynamics of Homogeneous Metal Carbonyl van der Waals Clusters

Fe(CO)₅ van der Waals Clusters. Perhaps the earliest indications of the unusual photodissociation dynamics of cluster-bound organometallics came out of an investigation of the photoionization behavior of jet-cooled Fe(CO)₅ by Smalley and co-workers (27). Jet-cooled monomer from a seeded helium expansion was observed to undergo MPI following irradiation at 157 nm by an F₂ excimer laser, giving rise to the expected photoions (i.e., a very strong signal due to atomic metal ions, and very weak signals due to the iron mono- and dicarbonyl ions). At this wavelength, neutral

$\text{Fe}(\text{CO})_5$ clusters larger than the trimer were observed to undergo one-photon ionization, giving rise to a distribution of cluster ions of the type, $[\text{Fe}(\text{CO})_5]_n^+$.

Drastically different results were obtained following irradiation at 193 nm from an ArF excimer laser. At this wavelength, two sequences of cluster ion signals were observed by time-of-flight mass spectrometry: a major sequence, attributed by Smalley and co-workers to bare metal cluster ions, Fe_x^+ ; and a minor sequence, attributed to $\text{Fe}_x(\text{CO})_y^+$. Because ^{56}Fe (natural abundance 91.8%) has an atomic mass indistinguishable from twice the molecular mass of $^{12}\text{C}^{16}\text{O}$ (natural abundance 98.7%), it was not possible for Smalley and co-workers to assign a unique stoichiometry to any given cluster ion. They reasoned that since cluster ions containing odd numbers of CO ligands (and therefore falling between successive Fe_x^+ clusters) constitute only a small fraction of the total photoion yield, cluster ions containing even numbers of CO ligands probably constitute only a minor degree of isobaric interference. Photoion yields were found to be highly wavelength dependent; for example, MPI of the cluster beam at 266 nm failed to produce any significant cluster photoion signal. The photodissociation and ionization behavior of these van der Waals clusters is rather remarkable, since the photoproduct ion distribution implies extensive rearrangement of both strong (covalent) and weak (dispersive) bonds within the clusters following photoexcitation, and the pronounced wavelength dependence is observed over a narrow spectral region where absorption is diffuse.

Mo(CO)₆ van der Waals Clusters. Investigations of metal carbonyl van der Waals cluster photophysics in the SUNY laboratory began in late 1988 (28). Mo(CO)₆ was chosen for initial experiments for two reasons. First, much was already known about the one-photon photodissociation dynamics of the Group VIB hexacarbonyls in both gas and condensed phases, offering a body of existing knowledge upon which to build. Second, although the photodissociation dynamics of clusters of $\text{Fe}(\text{CO})_5$ had

received a certain amount of attention, clusters of homoleptic metal carbonyls from other triads had not yet been examined. Given the ready availability of the hexacarbonyls of chromium, molybdenum, and tungsten, it might then be possible to study the systematics of intracluster photochemistry in a series of analogous metal carbonyls. Although the quadrupole mass analyzer originally employed for photoproduct ion detection in the pulsed molecular beam apparatus was limited in terms of sensitivity and mass range, it enabled the collection of both electron-impact and MPI mass spectra of the Mo(CO)₆ cluster beam.

Mass Spectroscopic Analysis of the Mo(CO)₆ Cluster Beam. Mass spectra of the Mo(CO)₆ cluster beam collected following either electron impact or multiphoton ionization are shown in Figure 1. The electron impact mass spectra for the cluster beam and for an effusively introduced sample of Mo(CO)₆ were indistinguishable over the m/z range illustrated. The signals observed correspond to the daughter ions expected following prompt statistical decay of nascent Mo(CO)₆⁺ parent ions. The MPI mass spectrum of naked Mo(CO)₆ is dominated by atomic metal ions and, as expected, displays no signals due to molecular ionization. The MPI mass spectrum of the Mo(CO)₆ cluster beam, however, displays totally unexpected features, which were attributed to the formation of metal oxide ions.

Possible Origins of the Metal Oxide Photolons. What is the mechanism by which these ions arise, and what inferences may be derived regarding cluster photophysics? From the dependence of the metal oxide ion signal upon the relative timing of the photoionizing laser and the molecular beam pulse, and from the absence of metal oxide ions in the MPI spectrum of naked Mo(CO)₆, we deduced that these unexpected photoions were arising from species present in the molecular beam rather than from oxygen-containing impurities in the vacuum chamber. However, no oxygen-con-

taining species other than the carbonyl ligands themselves could be detected in the molecular beam gas mixture. This implied that some unusual bimolecular chemical reaction was taking place among metal carbonyl species in the molecular beam. Reactions occurring fast enough to reach completion within the ca. 20-nanosecond duration of the laser pulse would be most likely if they were occurring between molecules *within* individual van der Waals clusters. We concluded that these intra-cluster reactions probably involved two neutral partners, rather than an ion and a neutral, since evidence of this bimolecular reactivity (i.e., appearance of metal oxide fragment ions) was noticeably absent following electron impact excitation. (Electron impact excitation of $\text{Mo}(\text{CO})_6$ gives rise to a series of coordinatively unsaturated *ionic* species, while photodissociation gives rise to *neutral* molecular species.)

We speculated that irradiation of van der Waals clusters containing $\text{Mo}(\text{CO})_6$ leads to production of cluster-bound, coordinatively unsaturated molybdenum carbonyl species. Such a photoproduct may utilize vacancies in its coordination sphere to accommodate one or more oxygen atoms from the carbonyl ligands of an adjacent $\text{Mo}(\text{CO})_6$ molecule within the cluster. Although this mode of CO coordination involving symmetric bridging and four-electron donation is unusual, it is not without precedent in synthetic organometallic chemistry (29-31). Coordinatively unsaturated molybdenum carbonyls are known to undergo analogous bimolecular reactions with $\text{Mo}(\text{CO})_6$ in the gas phase, although the structures of these dinuclear adducts are unknown (32). It was inferred that such a dinuclear adduct, when formed within the confines of a van der Waals cluster, can be subsequently photoionized and dissociated, giving rise to the observed metal oxide photoions. A cyclic adduct containing two bridging carbonyls might account for the appearance of both mono- and dioxomolybdenum photoions. It is surprising that complete ligand stripping of the inferred adduct does not take place, and that photoinduced activation of the C-O bond does. The strength of the C-O bond in such a symmetrically bridging carbonyl ligand should be considerably

weaker than that of free CO. In fact, in the chemisorption of CO to Cr and Mo crystals in which the CO internuclear axis lies parallel to the metal surface, C-O stretching frequencies between 1000 and 1300 cm⁻¹ have been observed (33,34). This mode of surface adsorption probably involves metal-ligand bonding somewhat analogous to that suggested for the cluster-bound adduct.

Cr(CO)₆ and W(CO)₆ van der Waals Clusters. The assumption that the dinuclear adduct formed following photoexcitation of an Mo(CO)₆ cluster is a six-membered metallacycle, containing two Mo atoms symmetrically bridged by two CO ligands, led us to predictions about intracluster photochemical behavior for clusters of other Group VIB hexacarbonyls (35). Given that the bridging carbonyls must be kept far enough apart to prevent overlap of filled CO π -orbitals within the plane of and protruding into the interior of the ring, there exists a limited range of metal-carbon and metal-oxygen bond lengths which can be accommodated within the constraints of the proposed metallacycle structure. While known metal-oxygen bond lengths for both tungsten- and molybdenum-containing organometallic species fall within this range, typical chromium-oxygen single-bond lengths are about 0.1 Ångstrom too short. We predicted that photoexcitation of W(CO)₆ clusters might lead to intracluster production of a dinuclear metal carbonyl having the cyclic structure suggested for the Mo(CO)₆ system, but that photoexcitation of Cr(CO)₆ clusters would not (although a dinuclear chromium-containing adduct with some alternative structure certainly might be produced). It is interesting to note the resulting photoion yields following 248-nm MPI of cluster beams of W(CO)₆ and Cr(CO)₆. We observed the appearance of the anomalous metal oxide photoions in the former case, but not in the latter case (35). These observations lend credence to our structural model and inferences regarding metal carbonyl intracluster photochemistry.

Evidence from studies of metal carbonyl van der Waals cluster MPI suggests

that the photophysical behavior of cluster-bound metal carbonyls is significantly different from that of naked organometallic molecules. It is quite remarkable that irradiation of these clusters does not result in evaporative dissociation of the cluster into its individual monomeric subunits, and that complete ligand stripping does not appear to precede photoionization. These inferences were formed on the basis of some very indirect observations. We were able to detect only those photofragment ions of fairly low m/z , and sensitivity was limited. Detection of primary intracluster photoproducts was complicated by the possibility of intracluster bimolecular reactions. In order to probe more directly the fundamental photophysical processes occurring in clusters containing metal carbonyls, we turned our attention to heterogeneous van der Waals clusters. Such clusters can form in the free jet expansions of gas mixtures containing a buffer gas (helium, for example) seeded with a small proportion of the metal carbonyl as well as a much larger proportion of some "solvent" molecule. Depending on the relative proportions of organometallic and solvent molecules in the beam gas mixture, the likelihood of forming clusters with more than one or two organometallic molecules per cluster is diminishingly small. The probability of intracluster bimolecular reactions between organometallic species is reduced, and complications from such reactions are thereby mitigated. We employed a time-of-flight mass spectrometer with single-ion detection capability to monitor cluster photoions, thus allowing greatly improved mass range and sensitivity. These experiments are described below.

Photodissociation Dynamics of Heterogeneous Metal Carbonyl van der Waals Clusters

Studies of the multiphoton ionization and fragmentation dynamics of metal carbonyl-containing heteroclusters were carried out using a differentially-pumped molecular beam time-of-flight mass spectrometer (R. M. Jordan Company). We chose to examine

heteroclusters composed of $\text{Cr}(\text{CO})_6$ and methanol (36,37). Methanol was chosen as a solvent molecule for two important reasons. First, methanol by itself was found to cluster quite easily, forming homogeneous clusters containing as many as a few dozen molecules. Second, nonresonant MPI of methanol clusters had already been well-characterized (38). The photoionization mass spectrum for the pure methanol clusters is fairly uncomplicated, consisting of ion signals attributed to the intracluster ion-molecule reaction products, $(\text{CH}_3\text{OH})_n\text{H}^+$ and $(\text{CH}_3\text{OH})_n(\text{H}_2\text{O})\text{H}^+$. $\text{Cr}(\text{CO})_6$ was preferred as the metal carbonyl component of the heteroclusters since the distribution of naturally-occurring chromium isotopes (^{52}Cr , 83.79%; three other isotopes, each less than 10%) simplified the interpretation of the mass spectra.

One of the questions we wished to address in studying the MPI of $\text{CH}_3\text{OH}/\text{Cr}(\text{CO})_6$ heteroclusters involves the competition between photodissociation of metal-ligand bonds and photoionization of molecular species. Does multiphoton excitation of a cluster-bound metal carbonyl lead to the cleavage of all metal-ligand bonds and the eventual appearance of solvated atomic ions, or does it lead alternatively to the production of metal carbonyl photoions? If cluster-bound $\text{Cr}(\text{CO})_6$ were to behave like naked $\text{Cr}(\text{CO})_6$ in the gas phase, one would expect that ligand loss would be extensive, and that the heterocluster MPI mass spectrum would be dominated by signals due to solvated chromium ions. If, on the other hand, cluster-bound $\text{Cr}(\text{CO})_6$ were to behave like $\text{Cr}(\text{CO})_6$ in condensed (solution or matrix) phases, ligand loss from neutral $\text{Cr}(\text{CO})_6$ would be less extensive, and production of metal carbonyl photoions would be likely. As discussed below, the dynamics of multiphoton dissociation and ionization was observed to be intermediate between these two extremes.

Cluster MPI Following 248-nm Irradiation at Moderate Fluence. We first examined the photoion yields following low-fluence 248-nm MPI of $\text{CH}_3\text{OH}/\text{Cr}(\text{CO})_6$ heteroclusters (36). A portion of the MPI mass spectrum collected following irradiation of

the cluster beam at 2×10^7 W/cm² is shown in Figure 2. It is immediately apparent that the observed photoions do not correspond simply to solvated chromium ions, but represent instead a series of solvated, coordinatively unsaturated metal carbonyl ions with the empirical formula, $S_nCr(CO)_x^+$, where S represents a methanol molecule and $x = 0, 1, 2, 5, 6$. We suggested that the mechanism for formation of these cluster ions does *not* involve initial photoionization of methanol, since neat methanol clusters could not be efficiently ionized by irradiating at the mild intensities employed here. Rather, these cluster ions appear due to photoionization of some cluster-bound chromium carbonyl species. The solvated penta- and hexacarbonyl ions appear for $n+x \geq 7$, while the remaining cluster ions appear for $n+x \geq 6$. Assignments of cluster ions were confirmed by examining photoion yields from MPI of a CD₃OD/Cr(CO)₆ heterocluster beam. Almost all of the chromium-containing cluster ions observed could be attributed to solvated *mononuclear* chromium carbonyl species, although some of the weaker ion signals at higher m/z were tentatively identified as *dinuclear* species.

One might imagine two alternative routes to the production of the metal carbonyl-containing cluster photoions. These two mechanisms can be experimentally distinguished, since the yield of photoions arising via the first mechanism should display a *different* dependence on the photoionization laser wavelength than the yield of photoions arising via the second mechanism. In the first mechanism, solvated Cr(CO)₆ is directly photoionized, and the distribution of coordinatively unsaturated metal carbonyl ions observed in the mass spectrum arise from fragmentation of this hexacarbonyl parent ion. The observation of solvated hexacarbonyl ions in the mass spectrum in Figure 2 indicates that at least *some* of the photoions must be produced by this mechanism. Under conditions of extremely high photoionizing laser fluence (e.g., 10^{13} W/cm²), secondary photofragmentation of these solvated hexacarbonyl parent ions should be extensive, and the distribution of daughter photoion clusters should be insensitive to the laser's wavelength. Alternatively, these ions may form via a second

mechanism. Some *neutral*, coordinatively unsaturated chromium carbonyl species, bound within a cluster of methanol molecules, may form following photodissociation of the solvated $\text{Cr}(\text{CO})_6$. This neutral photoproduct may then be subsequently photoionized, eventually fragmenting into a series of solvated daughter ions. If the identity of the cluster-bound, *neutral* photoproduct depends on laser wavelength (as is the case for dissociation of naked, gas-phase $\text{Cr}(\text{CO})_6$), then one might expect ion yields following MPI of the $\text{CH}_3\text{OH}/\text{Cr}(\text{CO})_6$ heterocluster beam to display a dependence on photoionizing wavelength. The observation of such a wavelength dependence would indicate that the second alternative mechanism considered here is important in the MPI of the neutral heteroclusters.

Wavelength Dependence of Photolon Yields Following Heterocluster MPI. Photoion yields following 248-nm MPI and 350-nm MPI of the $\text{CH}_3\text{OH}/\text{Cr}(\text{CO})_6$ heterocluster beam were compared. At each wavelength, laser fluence was about 10^{13} W/cm². (Strong focusing was necessary at 350 nm in order to produce reasonable photoion signal, and was employed at 248 nm to facilitate comparison of the two spectra.) The 248-nm mass spectrum displays a sequence of peaks attributed to solvated chromium ions, and a second sequence attributed to cluster ions containing chromium and water. Water is known to be created in intracluster ion-molecule reactions in neat methanol cluster ions (*vide supra*). By contrast, the 350-nm mass spectrum displays a sequence of peaks attributed to solvated $\text{Cr}(\text{CO})_5^+$, a second attributed to solvated $\text{Cr}(\text{CO})_4^+$, and a third attributed to cluster ions containing both $\text{Cr}(\text{CO})_5^+$ and water.

If MPI at 248 nm gave rise to the same *primary* photoion as MPI at 350 nm, and if subsequent fragmentation of this parent photoion were rigorously described by a statistical model, then one would expect the observed distribution of daughter photofragment ions to depend on the *total photon energy*, rather than the wavelength of the ph-

tons, absorbed by the nascent parent ion. Under conditions of strong focusing and extremely high laser fluence, one might therefore expect the two mass spectra to display nearly identical fragmentation patterns. The fact that these two spectra are *not* similar suggests that the primary photoion produced following 248-nm MPI is not the same as that produced following 350-nm MPI. Differences in the mass spectra may be accounted for by analogy with known single-photon dissociation behavior of naked Cr(CO)₆ in the gas phase. It is known that vibrationally excited Cr(CO)₄ is the major primary photoproduct of the 248-nm, single-photon dissociation of Cr(CO)₆ in the gas phase, while Cr(CO)₅ is the major primary photoproduct at 351 nm (39). It was suggested that single-photon dissociation of Cr(CO)₆ within methanol clusters might display the same wavelength dependence and give rise to the same (cluster-bound) coordinatively unsaturated photoproducts as are observed in simple gas-phase photodissociation (37). MPI of the CH₃OH/Cr(CO)₆ heterocluster beam was suggested to proceed *not* by initial ionization of Cr(CO)₆, but rather by initial formation of a *neutral* single-photon dissociation product within the cluster, followed by MPI of this solvated, coordinatively unsaturated species. Fragmentation of the nascent parent ion would then depend upon its internal energy. It was estimated that photoionization of hot Cr(CO)₄ (the photoproduct of 248-nm dissociation of solvated Cr(CO)₆) would require two additional 248-nm photons and would lead to a solvated Cr(CO)₄⁺ parent ion with as much as 103 kcal/mol of internal energy; while photoionization of hot, solvated Cr(CO)₅ (the 350-nm single-photon photoproduct of solvated Cr(CO)₆) would require two additional 350-nm photons, but would lead to a solvated Cr(CO)₅⁺ parent ion with only 21-36 kcal/mol of internal energy (37). One would then expect subsequent fragmentation of the nascent parent ion to be extensive following 248-nm MPI, but much less extensive (perhaps limited perhaps to loss of a single additional CO ligand) following 350-nm MPI. This predicted behavior is consistent with that observed in the mass spectra.

REMPI Spectroscopy of Cluster-Bound Metal Carbonyls. It was possible in the experiments described above to use a single pulse from the excimer-pumped dye laser (tuning range 346-371 nm) both to photolytically prepare solvated Cr(CO)₅ and to resonantly photoionize this pentacarbonyl (37). Photoion signal from a Cr(CO)₅⁺-containing cluster ion was monitored while slowly stepping the laser wavelength through the tuning range of the dye. The resulting REMPI spectrum corresponds to an optical absorption spectrum of the neutral pentacarbonyl, displaying a resonant absorption feature which grows in at wavelengths shorter than about 353 nm and reaches a maximum somewhere outside the blue limit of the laser dye. Neat methanol clusters, by contrast, display a maximum in their REMPI spectra at about 362 nm. Since the Cr(CO)₅⁺-containing cluster ions display no such resonant feature at 362 nm, they must arise not by initial photoionization of a methanol molecule within the cluster, but rather by ionization of a chromium carbonyl species.

Participation of Solvent Molecules in Energy Disposal. It is not possible in the cluster MPI experiments described here (36,37) to assess directly the importance of introcluster collisional relaxation or evaporation of solvent molecules as energy disposal mechanisms. It appears, however, that in the initial single-photon dissociation of solvated Cr(CO)₆, transfer of excess energy from excited photoproducts to the solvent bath is not as efficient as in the case of condensed-phase photodissociation. If introcluster energy transfer to the solvent bath were highly efficient, one might expect to see typical condensed-phase behavior; i.e., single-photon absorption always leading to single-ligand loss. Solvent evaporation may be important in the disposal of excess energy from cluster ions. We noted that in general, the daughter ions produced following MPI of CD₃OD/Cr(CO)₆ heteroclusters display a lesser degree of fragmentation than those produced following MPI of CH₃OH/Cr(CO)₆ heteroclusters (Peifer, W. R.; Garvey, J. F. In *Isotope Effects in Gas Phase Chemical Reaction and*

Photodissociation Processes; Kaye, J., Ed.; ACS Books: Washington, D.C., in press). For example, both solvated $\text{Cr}(\text{CO})_5^+$ and solvated $\text{Cr}(\text{CO})_4^+$ photoions appear following 350-nm MPI of $\text{CH}_3\text{OH}/\text{Cr}(\text{CO})_6$ heteroclusters; but only the solvated pentacarbonyl photoions appear following 350-nm MPI of perdeuterated $\text{CD}_3\text{OD}/\text{Cr}(\text{CO})_6$ heteroclusters. This phenomenon was observed following MPI at other wavelengths, and over a broad range of laser fluences. Apparently, CD_3OD is more efficient than CH_3OH in collisionally relaxing excited chromium carbonyl photoions produced within these heteroclusters. It was suggested that intracluster energy transfer from an excited metal carbonyl photoion to a surrounding solvent molecule can occur through a highly non-statistical mechanism, provided that: (a) the energy defect between the appropriate internal modes of the excited photoion and the adjacent solvent molecule is very small; and (b) the transfer of energy from the donor mode to the acceptor mode is not symmetry-forbidden. It is remarkable that intracluster energy transfer takes place in such an apparently non-statistical manner. These heteroclusters may constitute an interesting experimental model in which to study the dynamics of intracluster energy partitioning and disposal.

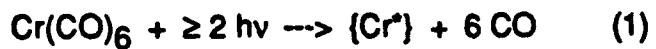
Future Directions -- Probing the Electronic Structure of Naked Organometallics in the Gas Phase

All of the experiments described above involve detection and characterization of organometallic photoproducts trapped within van der Waals clusters. While much information on the electronic structure and dynamics of open-shell organometallics can be learned from such studies, it would be desirable to develop probes for the interrogation of naked, open-shell organometallic species in the gas phase. The availability of such probes would likely contribute to a better understanding of mechanistic organometallic chemistry, refinements in metal-organic chemical vapor deposition

(MOCVD) technology, and further insights into the multiphoton dissociation dynamics of and metal atom production from gas-phase organometallics. Toward this end, we have recently initiated a program of research on new time-resolved, two-laser techniques for organometallic photoproduct generation and characterization. A given coordinatively unsaturated organometallic is first produced by pulsed UV laser photolysis of an appropriate precursor, and a second laser pulse is then employed to induce multiphoton dissociation (MPD) of this photoproduct, yielding metal atoms in a distribution of electronic states. The state distribution of these atoms can be determined by atomic emission and LIF. The electronic temperature of the *atomic* photoproducts is directly related to the internal energy of the *molecular* photoproduct created by the first laser pulse. For cases where MPD of the precursor species and MPD of the coordinatively unsaturated molecular photoproduct lead to different metal atom state distributions, it then becomes possible to detect the presence of the photoproduct with a level of sensitivity not attainable with conventional IR absorption techniques such as TRIS.

In the remainder of this section, studies of the dynamics of the MDP of organochromium compounds, which provided the conceptual basis for the two-laser technique described above, will be briefly reviewed. Preliminary results from a study of the photodissociation dynamics of jet-cooled Cr(CO)₆ using the two-laser technique will then be presented.

Multiphoton Dissociation Dynamics of Cr(CO)₆. Tyndall and Jackson have studied the 248-nm MPD dynamics of Cr(CO)₆ using fluorescence detection of the atomic photoproducts (40). On the basis of fluorescence quenching results, they indirectly determined that two mechanisms exist for production of chromium atoms following 248-nm irradiation of Cr(CO)₆. These two mechanisms can be described as direct and sequential, and are represented in Reactions (1) and (2), respectively.



MPD via the direct mechanism, represented in Reaction (1), gives rise to a statistical distribution of chromium electronic states characterized by a high temperature. Fluorescence from high-lying electronic states is found to be insensitive to the pressure of added buffer gas in the photolysis cell. However, MPD via the sequential mechanism, depicted in Reactions (2a) and (2b), proceeds through the intermediacy of a coordinatively unsaturated species (in this case, vibrationally excited $\text{Cr}(\text{CO})_4$) and gives rise to low-lying states of chromium atoms characterized by a much lower electronic temperature. LIF signals pumped from non-emitting, low-lying states can be quenched by addition of buffer gas to the photolysis cell. Furthermore, it has been shown that in the *sequential* (but not the *direct*) MPD of organochromium precursors containing a variety of polyatomic ligands, the electronic temperature of the resulting atomic photoproducts is inversely related to the vibrational state density of the molecular photoproduct's ligands (41,42). The fact that the $\text{Cr}(\text{CO})_4$ intermediate's internal energy is reflected in the electronic temperature of the chromium atoms produced from the subsequent photodissociation of $\text{Cr}(\text{CO})_4$ forms the conceptual basis of a two-laser technique to probe molecular photoproduct internal energy, electronic structure, and relaxation dynamics.

Effect of Precursor Temperature on 248-nm $\text{Cr}(\text{CO})_6$ MPD Dynamics. In recent experiments at SUNY, we have examined the MPD dynamics of jet-cooled $\text{Cr}(\text{CO})_6$, and compared the resulting chromium state distribution with that obtained following MPD of room-temperature $\text{Cr}(\text{CO})_6$ in a gas cell experiment (Peifer, W. R.;

Garvey, J. F.; DeLeon, R. L. *J. Chem. Phys.*, submitted). Portions of the dispersed fluorescence spectra collected following MPD of both room-temperature and jet-cooled Cr(CO)₆ are shown in Figure 3. Emission signals in these spectra assigned to the septet system originate from excited chromium atoms prepared by direct MPD of Cr(CO)₆, while signals assigned to the quintet system originate from 248-nm LIF excitation of the two lowest quintet terms of chromium. These low-lying quintets are prepared by sequential MPD of Cr(CO)₆, through the intermediacy of an excited Cr(CO)₄ primary photoproduct. It is important to note that initial photodissociation of Cr(CO)₆, subsequent photodissociation of Cr(CO)₄, and final LIF excitation of the low-lying quintet terms of the chromium photoproduct, are all accomplished within the duration of a single 248-nm excimer laser pulse (20-nsec FWHM gaussian). While room-temperature Cr(CO)₆ appears to photodissociate through both the direct and sequential pathways, the fluorescence spectrum acquired following MPD of jet-cooled Cr(CO)₆ shows none of the quintet features indicative of sequential MPD.

One might expect the quintet signals to be quenched if the primary Cr(CO)₄ photoproduct were collisionally relaxed. However, number densities in the probed portion of the molecular beam were calculated to be too low for collisional quenching to be likely (43), and no evidence of radiation trapping, which might be expected under conditions of high number density, was revealed in measurements of excited state lifetimes. Given that excited Cr(CO)₄ is the primary 248-nm photoproduct of jet-cooled Cr(CO)₆ (44,45), the failure to observe evidence of sequential 248-nm MPD of jet-cooled Cr(CO)₆ seems most likely due to a slower rate of appearance of the excited Cr(CO)₄ photoproduct in the molecular beam. If Cr(CO)₄ does not appear within about 20 nanoseconds following initial photodissociation of the jet-cooled hexacarbonyl precursor (after which time the pulse of laser photons has passed), it cannot be detected by the atomic fluorescence technique.

Time-resolved Technique for Molecular Photoproduct Detection. If indeed $\text{Cr}(\text{CO})_4$ is produced from 248-nm photolysis of jet-cooled $\text{Cr}(\text{CO})_6$ at a slower rate than from photolysis of the room-temperature hexacarbonyl, then one should be able to detect it by irradiating the molecular beam with a second laser pulse which is delayed with respect to the first pulse. Slowly evolving $\text{Cr}(\text{CO})_4$ created following initial photolysis of the jet-cooled hexacarbonyl should then be dissociated by the second pulse into the characteristic state distribution of chromium atoms, and emission lines in the quintet system associated with sequential MPD should once again appear in the fluorescence spectrum. The results of such a two-laser, time-resolved experiment are illustrated in the fluorescence spectrum in Figure 4. This spectrum was acquired by initial single-photon dissociation of jet-cooled $\text{Cr}(\text{CO})_6$ at 222 nm, producing roughly equal amounts of $\text{Cr}(\text{CO})_3$ and $\text{Cr}(\text{CO})_4$ (23). These molecular photoproducts were then photodissociated at 248 nm by the pulse from a second excimer laser which was delayed 300 nanoseconds with respect to the first pulse. The quintet emission features characteristic of sequential MPD of the jet-cooled hexacarbonyl are once again visible. It is important to note that these features appear only for delay times longer than about 60 nanoseconds, reaching maximum intensity for delays greater than about 200 nanoseconds. The temporal profile for the growing in of these quintet signals can be fitted by a simple rising exponential with a 40-nanosecond time constant, convoluted with the integral of the first laser's temporal profile. Eventual decay of these quintet signals for delays in excess of one or two microseconds can be modeled simply in terms of the escape of primary molecular photoproducts from the photolysis probe volume at the nominal molecular beam velocity.

Implications for Photodissociation Dynamics. It is not presently clear why the rate of production of $\text{Cr}(\text{CO})_4$ from photolysis of a jet-cooled precursor should be slower than from photolysis of a room-temperature precursor. Vernon and coworkers

ers have suggested that the mechanism for production of Cr(CO)₄ following 248-nm photolysis of jet-cooled Cr(CO)₆ proceeds in three steps: non-statistical ejection of the first CO ligand; internal conversion of the nascent, electronically excited pentacarbonyl to its ground electronic surface; and finally, statistical loss of the second CO ligand (45). According to the calculations of Hay (46), the ground and first excited states of the pentacarbonyl are vibronically coupled through low-energy OC-M-CO bending modes. If these modes are not populated in the nascent pentacarbonyl, then the internal conversion step should occur at a slower rate. It is tempting to speculate that these modes cannot be directly populated by the one-photon absorption (and dissociation) process used to prepare the pentacarbonyl. In such a case, the only way these modes will be populated in the nascent pentacarbonyl is if the correlated bending modes are already populated in the hexacarbonyl precursor. One would expect that in a 300K molecule of Cr(CO)₆, such correlated modes *would* be thermally populated, whereas in a jet-cooled molecule of Cr(CO)₆, even these low-energy modes *would not* be significantly populated.

Concluding Remarks

The UV and near-UV laser techniques described in this chapter represent promising new approaches for the study of the electronic structure of open-shell organometallics, and the influence of excited electronic states on the dynamics of single- and multiphoton dissociation. The encapsulation of organometallic molecules within van der Waals clusters not only allows one to employ powerful laser-based probes for spectroscopic studies, but may provide the experimentalist with convenient models for the study fast *dynamical* processes such as intermolecular energy transfer within the quasi-condensed state.

Studies on the time-resolved, two-laser sequential MPD of transition metal car-

bonyls are continuing in our laboratory. This technique is characterized by sensitivity far better than that obtainable with transient absorption techniques, is not limited in terms of the identity of the attached ligands, and has the potential for superior temporal resolution (due to the use of visible rather than IR-sensitive detectors). Of particular interest is the influence of the electronic state of the intermediate molecular photoproduct on the state distribution of the subsequent atomic photoproduct. The ability to selectively prepare and detect specific excited states of naked, open-shell metal carbonyls may eventually allow for great advances in the study of mechanistic organometallic chemistry.

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Figure 1. Mass spectra of $\text{Mo}(\text{CO})_6$, 40-200 amu. Ion signals for the three spectra are in arbitrary units and are not normalized with respect to each other. Signals at 52 and 56 amu are due to trace impurities of Cr and Fe. (A) Electron impact ionization mass spectrum of $[\text{Mo}(\text{CO})_6]_n$ van der Waals cluster beam. (B) MPI mass spectrum of $\text{Mo}(\text{CO})_6$ monomer in a gas cell. (C) MPI mass spectrum of $[\text{Mo}(\text{CO})_6]_n$ van der Waals cluster beam. (Reproduced from ref. 28.)

Figure 2. Low-fluence 248-nm MPI mass spectrum of $(\text{CH}_3\text{OH})/\text{Cr}(\text{CO})_6$ heterocluster beam, 250-475 amu. Integers above the peaks correspond to values of n , the number of CH_3OH molecules in an individual cluster ion. (Reproduced with permission from ref. 36. Copyright 1991 American Institute of Physics.)

Figure 3. Atomic fluorescence spectra collected following 248-nm MPD of $\text{Cr}(\text{CO})_6$. Term symbols for the emitting states of Cr are indicated across the top of the figure. Spectral features assigned to the septet system are due to emission from excited states of Cr, which appear following concerted MPD of $\text{Cr}(\text{CO})_6$. Spectral features assigned to the quintet system are LIF transitions pumped out of the a^5S and a^5D states of Cr, which arise from sequential MPD of $\text{Cr}(\text{CO})_6$. Upper spectrum: MPD of $\text{Cr}(\text{CO})_6$ at 300K in gas cell. Lower spectrum: MPD of jet-cooled $\text{Cr}(\text{CO})_6$.

Figure 4. Atomic fluorescence spectrum collected following two-laser MPD of jet-cooled $\text{Cr}(\text{CO})_6$. The hexacarbonyl was first photodissociated at 222 nm, and the coordinatively unsaturated photoproducts were probed 300 nanoseconds later by further photodissociating at 248 nm to a distribution of atomic states of Cr. Intense LIF emission in the quintet system, indicative of sequential MPD of $\text{Cr}(\text{CO})_6$, is observed for delays exceeding 60 nanoseconds.

